

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Treating Oxide-Coated Aluminium Surfaces

We, CHARLES CALVIN COHN and SAMUEL LENARD COHN, both citizens of the United States of America, and trading in co-partnership as COLONIAL ALLOYS COMPANY of Avenue and Crawford Street, City of Philadelphia, Commonwealth of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the covering of the surfaces of aluminum and aluminum base alloys, herein collectively designated as aluminum, with a coating capable of resisting the actions of corrosive agencies. The invention particularly contemplates the provision on said aluminum surfaces of a corrosion resistant oxide coating.

By various known processes aluminum surfaces may be provided with what is generally termed an "oxide coating." Such a coating is composed in large part of aluminum oxide. As stated, the coatings may be produced by various methods, which methods, with few exceptions, comprise a reaction, chemical or electrochemical, between the aluminum surface and a solution of a chemically active substance or substances. The present invention refers to coatings which are produced by these artificial means and which are adsorptive. The very thin film of oxide naturally forming on aluminum surfaces is not herein referred to as an oxide coating.

One useful treatment of oxide-coated aluminum surfaces is to color the coating either by depositing therein a substance of characteristic color or by treating the oxide-coated surface with a solution of an organic dye which is adsorbed in or on the coating and produces a characteristic color. Another useful treatment of oxide-coated aluminum surfaces is to deposit in the coating, whether or not the latter is colored, a corrosion-inhibiting substance, which seals the coating and increases the corrosion resistant property of the coating.

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It is known to effect sealing of the oxide coating by utilizing an aqueous solution containing a salt of a weak metallic base, such as nickel acetate or cobalt acetate, and it is known to effect sealing by utilizing an aqueous solution containing a soluble silicate, such as sodium silicate or potassium silicate. It is even known to effect sealing by utilizing plain hot water.

A hot water seal hydrates the oxide coating, in consequence of which the diameter of the coating pores and the area of the aluminum surface exposed through the pores to corroding media are decreased. The common practice is to make the oxide coating relatively thick because the thicker the coating, the greater the resistance to corrosion. Unfortunately, however, the coating also becomes softer with increased thickness, due to the protected period of time during which the electrolyte is in contact with the coating. The electrolyte attacks the coating, which is softened thereby.

Certain seals, for example, nickel and cobalt acetate seals, have the recognized ability to set a dye in a dyed oxide coating, to minimize bleeding of the dye from the oxide coating and to increase the light fastness of the dye, but they have no marked ability to increase the alkali or salt-spray corrosion resistance of an oxide coating. Certain other seals, for example, sodium and potassium silicate seals have the recognized ability to increase salt-spray corrosion resistance, but they have no marked ability to increase the alkali corrosion resistance of an oxide coating. The hot water seal has the recognized ability to decrease permeability of the coating, thus increasing corrosion resistance to certain media and decreasing the possibility of staining, but, as indicated hereinabove, for the hot water seal to be effective the coating treated must be comparatively thick. Accordingly, an important object of the present invention is the provision of oxide-coated aluminum articles having both increased salt-spray corrosion resistance and increased alkali corrosion resistance.

Another object of the present invention is

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the provision of oxide-coated aluminum articles having such corrosion resistance whether or not the oxide coating is colored.

5 Still another object of the present invention is the provision of oxide-coated aluminum articles having very thin colored or uncolored oxide coatings and such corrosion resistance.

Sealing in one step utilizing a salt of a weak metallic base, for example, nickel acetate, is characterized by the formation of undesirable smuts on the work, which smuts commonly are removed by buffing—an expensive operation. Accordingly, a further object of the invention is the provision of a sealing method including a treatment for eliminating such smuts, and, if desired, for providing the work with an etched or matte (non-reflective) surface having a distinctive decorative appearance.

20 Sealing a dyed oxide coating in one step utilizing a soluble silicate, for example, sodium silicate, is characterized by loss of the dye. Accordingly, a still further object of the invention is the provision of a sealing method including a treatment eliminating such dye loss and making possible alkali corrosion resistant colored oxide coatings.

In the practice of the invention an oxide coating is first formed on the aluminum in any one of numerous conventional ways, as by anodizing or chemical oxidation treatment. As is well-known, coatings varying in porosity may be produced, and the procedure chosen is that suitable for the end results desired; 30 for example, if coloring is to be involved, it will generally be desirable to provide more pervious coatings. The oxide-coated aluminum surface is then rinsed, and if a colored coating is desired, it is immersed in, or otherwise treated with, a solution of an organic dye, or a colored inorganic pigment is precipitated in the pores of the coating. The oxide-coated aluminum surface, whether dyed or undyed, is rinsed and then subjected to the two-step sealing procedure constituting the invention, which procedure in its preferred form is as follows:

The oxide-coated aluminum is immersed in a hot or boiling solution, i.e., a solution heated above 40° C., containing a salt of a weak metallic base, which salt is capable of hydrolyzing in solution having a pH of 4.5 to 7.5 to form a substantially insoluble compound of the metal in the oxide coating. The treatment is in all respects in accordance with the teaching of Patent No. 413,814 to which reference may be had for details of procedure and also for the hydrolyzable salts which may be used, nickel and cobalt, salts, for example, nickel acetate and cobalt acetate, being those ordinarily used in commercial practice. It should be noted, however, that hydrolysis may be such that suspension of colloidal dimensions is formed in the solution and no precipitate is evident. But if, on heating, a precipi-

tate is evident, the hydrogen ion concentration is so adjusted that a substantial amount of the metallic base is not precipitated in flocculent form and does not settle from the solution. In solutions where, on hydrolysis, precipitation is evident, it is desirable that the hydrolysis does not substantially proceed past the point of turbidity. The term "turbidity" as used herein and in the appended claims denotes not only a turbid but likewise an opalescent or cloudy solution. The oxide-coated aluminum is now ready for the second step of the method. After rinsing, the oxide-coated aluminum is treated with an aqueous solution of soluble silicate in which the ratio of silica to Na<sub>2</sub>O is not less than about 2:1 if etching is not desired. This second treatment is in all respects in accordance with the teaching of United States Letters Patent No. 1,946,153 or No. 2,161,636, to which patents reference may be had for details of compositions and procedures. Silicate may be adsorbed in the coating without forming a film over the coating; it may form a film over the coating without being absorbed in the coating. or it may be absorbed in the coating and also form a film over the coating. What actually happens is not readily apparent, in consequence of which, in the claims, the expression "absorbing in the coating" is intended to include any or all of these possibilities.

This invention accordingly consists in a method of treating aluminum articles to render the surfaces thereof both salt-spray and alkali corrosion resistant, comprising forming on the surface of the article an absorbent oxide coating, depositing in said oxide coating an insoluble compound by treating said article with an aqueous solution of a salt of a weak metallic base, and absorbing silicate in said coating by treating said article with an aqueous silicate solution.

Treating aluminum surfaces with a solution of a strong alkali or acid to etch the surface is known. But the treatment is administered before anodizing and the finish has a reflective, metallic luster. In accordance with the method of the invention, aluminum surfaces may now be treated after anodizing to provide the same with a matte, non-reflective distinct decorative appearance. The more alkaline the treatment solution, the greater the tendency to etch the surface. Therefore, a comparatively low ratio, for example, 1.6:1, of silica to soda or potash is utilized in the second step of the method of the invention when it is desired to create a matte, non-reflective finish. Alternatively, a higher ratio of silica to soda, for example, 2:1, or upwards, may be utilized, followed by treatment of the surface in a solution of high alkalinity, for example, dilute caustic soda, for a period of time sufficient for producing the desired effect. Of course, care must be exercised so that the oxide-coated aluminum is not un-

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desirably too extensively attacked by the treatment solutions. The proper treatment solution conditions for specific results may readily be determined by test, as by immersing several

- 5 pieces of oxide-coated aluminum in solutions of varying temperatures and concentrations, and for varying treatment periods and observing the results.
- 10 As an alternative to etching by the use of an alkaline treating material, the etching may be carried out, following the treatment with silicate to complete the sealing, by immersing the sealed surface in a dilute acid solution,
- 15 such as a dilute aqueous solution of phosphoric acid, or hydrochloric acid, or the like. A preferred bath for this purpose is one of 1% phosphoric acid in water used at room temperatures. Approximately three minutes of treatment are typically involved, though the
- 20 time, temperature and acid concentration may be widely varied depending upon the particular results desired.

Some suitable examples of commercial procedures may be given as follows:

#### EXAMPLE 1

- 25 Aluminum articles are anodically coated in a 15 per cent (by weight) sulfuric acid solution with a current density of 12 amperes per square foot of either alternating or direct current for from 5 to 60 minutes at 75° F., in
- 30 accordance with conventional practices. The articles are washed in water and then immersed in a 0.5 per cent (by weight) nickel acetate solution for from about 5 to about 20 minutes at a temperature of about 180° F.
- 35 The articles are washed in water again and then immersed in a 20 c.c./liter sodium silicate solution (silica to soda ratio of 2.4:1) for from about 5 to about 20 minutes at a
- 40 temperature of about 190° F. to 210° F. Times and temperatures indicated in the example are dependent upon thickness of the oxide coating originally produced, longer times being involved in the case of the thicker coat-
- 45 ings, and higher temperatures being desirably less than was involved, though the higher temperatures are even desirable in the case of thin coatings. If desired, the articles are washed once again in water. The result is a clear,
- 50 smutless uncolored oxide coating both salt-spray and alkali corrosion resistant regardless of whether the oxide coating is thick (0.0008 inch) or thin (0.0001 inch).

#### EXAMPLE 2

- 55 Aluminum articles anodically coated as described in Example 1 are washed and immersed in a dye bath containing 1 gram per liter of Alizarine Sapphire BN, of National Aniline Division, Allied Chemical Corpora-
- 60 tion. The dyed articles are then immersed in a 5 grams per liter nickel acetate solution for from about 5 to about 20 minutes at a temperature of about 180° F. The articles are washed in water again and then immersed in a
- 65 20 c.c./liter sodium silicate solution (silica to

soda ratio of 2.4:1) for from about 5 to about 20 minutes at a temperature of about 190° F. to 210° F. If desired, the articles are washed once again in water. The result is a blue oxide coating both salt-spray and alkali corrosion resistant, and, in addition resistant to dye bleeding or leaching. The same results are obtained whether the oxide coating is thick or thin. Here, again, times and temperatures may be chosen for the particular results desired, longer times being involved in the case of thicker coatings.

While a particular dye is referred to in the last example, the operation is typical of that involving any other of the many numerous dyes suitable for the coloring of aluminum oxide coatings. Such dyes are well-known to the art.

The sealed oxide coatings produced by the method of the present invention stand up for at least 16 hours when subjected to a salt-spray test carried out with an aqueous solution containing 5 per cent sodium chloride and 1 gram per gallon of cupric chloride, adjusted with acetic acid to a pH of 3.2, the solution being maintained at a temperature of 120° F. In addition, sealed oxide coatings produced by the method of the present invention stand up for from 8 to 10 minutes when immersed in an aqueous solution containing 3 per cent caustic soda, at room temperature.

As indicated, the method of the invention produces a clear, smutless uncolored oxide coating that is salt-spray and alkali corrosion resistant, regardless of the thickness of the coating. Treatment of an uncolored oxide coating with the first treatment solution containing a hydrolyzable weak metallic salt, for example, nickel acetate, leaves the otherwise clear oxide coating with characteristic smuts; but subsequent treatment of the marred oxide coating with a second treatment solution containing a soluble silicate causes the smuts to disappear.

The method of the invention, as indicated, also produces a colored oxide coating that is salt-spray and alkali corrosion resistant, regardless of the thickness of the coating. Treatment of a dyed oxide coating with a first treatment solution containing a soluble silicate removes the dye from the oxide coating, but such a treatment following a first treatment with a solution containing a hydrolyzable weak metallic salt, such as nickel acetate, which sets or insolubilizes the dye, does not remove the dye from the oxide coating.

The advantages of the method of the invention are realized even in the production of thin oxide coatings, in consequence of which great economies are effected in producing the oxide coating. The costs of labor, materials and electric power are reduced to a minimum. In addition, the hardness of the oxide coating is not sacrificed, and alkali, as well as salt-spray, corrosion resistance is attained. Since treat-

- ment of the oxide coating in accordance with the first step of the method of the invention alone produces practically no increase in alkali corrosion resistance and treatment of the oxide coating in accordance with the second step of the method of the invention alone produces no material increase in alkali corrosion resistance, it is not readily apparent why the combination of treatments should do so. However the fact remains that the combination of treatments does have the desired effect, which is of extreme importance because a great demand has arisen in certain industries for oxide-coated articles having both salt-spray and alkali corrosion resistance. In the automobile industry, for example, washing compounds for cleaning cars are sometimes very high in alkalinity, in consequence of which they have a tendency to corrode anodized aluminum parts. In the architectural field, the corrosive action of cements and mortars are often highly alkaline, tending to corrode anodized aluminum. Anodized aluminum, colored or clear, utilized for decorative purposes is usually attacked by alkali dishwashing solutions or the dye or other color is removed from the oxide coating. All these difficulties are eliminated by the two consecutive treatments in accordance with the invention.
- 30 WHAT WE CLAIM IS:—
1. In a method of treating aluminum articles to render the surfaces thereof both salt-spray and alkali corrosion resistant, the steps comprising forming on the surface of the article an adsorbent oxide coating formed from the metal surface, depositing in said oxide coating an insoluble compound by treating said article with an aqueous solution of a salt of a weak metallic base, and adsorbing silicate in said coating by treating said article with an aqueous silicate solution.
  2. The method set forth in claim 1 in which the silicate solution is maintained at a temperature above 80° C.
  3. The method set forth in claim 1 or 2 in which the solution of the salt of a weak metallic base is maintained at a temperature of at least 40° C.
  4. The method set forth in any of the preceding claims in which the salt of a weak metallic base is nickel acetate or cobalt acetate.
  5. The method set forth in any of the preceding claims in which the solution of the salt of a weak metallic base has a pH of 4.5 to 7.5.
  6. The method set forth in any of the preceding claims in which silicate is adsorbed in the oxide coating by treating the oxide coating in an aqueous solution of sodium silicate.
  7. The method set forth in claim 6 in which the oxide coating is anodically treated in the aqueous solution of sodium silicate.
  8. The method set forth in claim 6 or 7 in which the ratio of silica to sodium oxide in the aqueous solution of sodium silicate is not less than about 2:1.
  9. The method set forth in any of the preceding claims in which the oxide coating is not more than about 0.0001 of an inch thick.
  10. The method set forth in any of the preceding claims in which the oxide coated article is immersed in a solution of a salt of a weak metallic base in which hydrolysis proceeds to the point of turbidity and which contains no substantial amount of flocculent precipitate.
  11. The method set forth in any of the preceding claims which comprises forming an adsorbent oxide coating not more than about .0001 of an inch thick and imparting to the oxide coating a characteristic color by immersing the article in a bath containing an organic dye.
  12. The method set forth in any of the preceding claims in which after treatment with the aqueous silicate solution, the article is treated with a solution of high alkalinity to provide matte non-reflective surfaces.
  13. The method set forth in claim 12 in which the solution of high alkalinity is caustic soda.
  14. The method of treating aluminum articles substantially as hereinbefore described.
  15. The method of treating aluminum articles substantially as described with reference to Examples 1 or 2.
  16. Aluminum articles treated in accordance with the method of any of the preceding claims.
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